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Electrets

Selective Discharge of Electrostatic Charges on Electrets Using a Patterned Hydrogel Stamp**

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Electrets,[1] materials that can permanently store charge, have a long history in engineering and condensed-matter physics.[2] Recently, the field has drawn growing attention from the field of chemistry, especially after the hot debate between two renowned chemists, George Whitesides[2–5] and Allen Bard,[6–9] on the mechanism of contact electrification of dielectrics. Although the argument of charge transfer on tribocharging, either electrons or ions, is controversial and has not yet reached a consensus, the thorough investigation of the electrostatic phenomenon from both sides will still pave the way for other chemists and stimulate the exploitations for new application of electrets.

Patterning of electrostatic charges, as widely used in conventional xerography for many years, is attracting considerable interest because it is associated with strong electrostatic fields to control the behavior of nanoscale electronic and mechanical devices,[10] guide the assembly of nanomaterials,[11] or modulate the properties of biological systems.[12] High-resolution charge patterns can be produced either by injection of electrons into materials using electron beam lithography,[13] conducting atomic force microscopy,[14] and electrical microcontact printing,[15] or by printing of positive or negative ionic charges with electrohydrodynamic jetting.[16,17] One common ground for these advanced techniques is to selectively charge the electrets either by the inputting of electrons or ions, or by inducing and maintaining macroscopic electric dipoles by using a strong electric field.

In our previous study,[18] we proposed a much different approach in patterning of charge that involves the selective discharge of the electrostatic charges. We used a topographically patterned poly(dimethylsiloxane) (PDMS) stamp to transfer and print heat energy onto uniformly charged electrets, and the heat can neutralize the charges or release the dipoles through a thermally stimulated discharge or depolarization (TSD)[1] process to form patterns of charges. Hot microcontact printing (μCP), a simple and inexpensive procedure, is capable of patterning of electrostatic charges on bulk and thin-film electrets without needing to be supported on conductive substrates. Since many dielectrics can be charged through a simple contact electrification process that does not involve electric field, the selective discharge of electrostatic charges should be an enhanced way to achieve high-resolution charge patterns on electrets.

Herein, we propose another charge patterning approach based on the concept of selective discharge of electrostatic charges. Different from the academic TSD process, this new strategy stems from the practical observation that electrostatic charges are more stable in dry winter than in sultry summer conditions because humid air helps to dissipate electrostatic charges by keeping surfaces moist and increasing the conductivity. Herein, we use a topographically patterned hydrogel stamp to expose electrets purposely and selectively to water for discharging, hence leaving the electrostatic charges in the noncontacted area to achieve high-resolution charge patterns; by applying "single electrode" electrochemical reductions[6] in the charged area, we can also obtain a variety of metallic micro- or nanostructures on electrets.

Figure 1 a,b shows the procedure to fabricate the hydrogel stamp. Firstly, we prepared a PDMS stamp with topography preliminarily determined by photolithography. Then, agarose was molded against the PDMS relief structure to yield a stamp with an inverted bas-relief. Agarose has good mechanical stability combined with fast internal diffusion caused by a tunable water content of 20–98%; hence, hydrogel stamps have been widely used for the etching of metals,[19] printing of bacteria,[20] and fabrication of polymer microstructures by soaking of appropriate solutions.[21] Herein, the agarose hydrogel stamp was chosen for transferring and printing water onto electrets for the selective discharge of electrostatic charges.

Figure 1 c,d shows a typical process of charging electrets: A thin layer (100 nm) of poly(methylmethacrylate) (PMMA) film supported on a silicon wafer is uniformly charged under an electric field of $10\,\mathrm{kV\,cm^{-1}}$ by using aluminum foil as an electrode to apply electric potential. After applying pulsed voltage for 20 seconds, the PMMA electrets are uniformly charged, and the mechanism of this charging process is dominated to be the transport of electrons as explained by Jacobs and Whitesides.[15]

When uniformly charged electrets are contacted with the patterned hydrogel stamp as shown in Figure 1 e, the electrostatic charges (either electrons or ions) on the contacted part are removed through the diffusion from hydrogel stamp, whereas the charges on the untouched area remain, which results in high-resolution charge patterns. The patterns of charge, mainly electrons on PMMA electrets by this charging method, can reduce metal ions through electrostatic electro-

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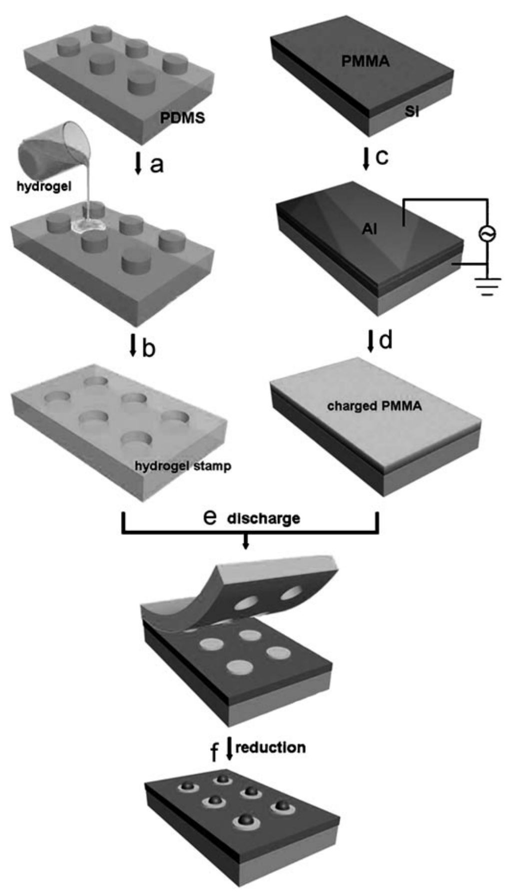

Figure 1. The procedure of electrostatic charge patterning using a hydrogel stamp. See text for details.

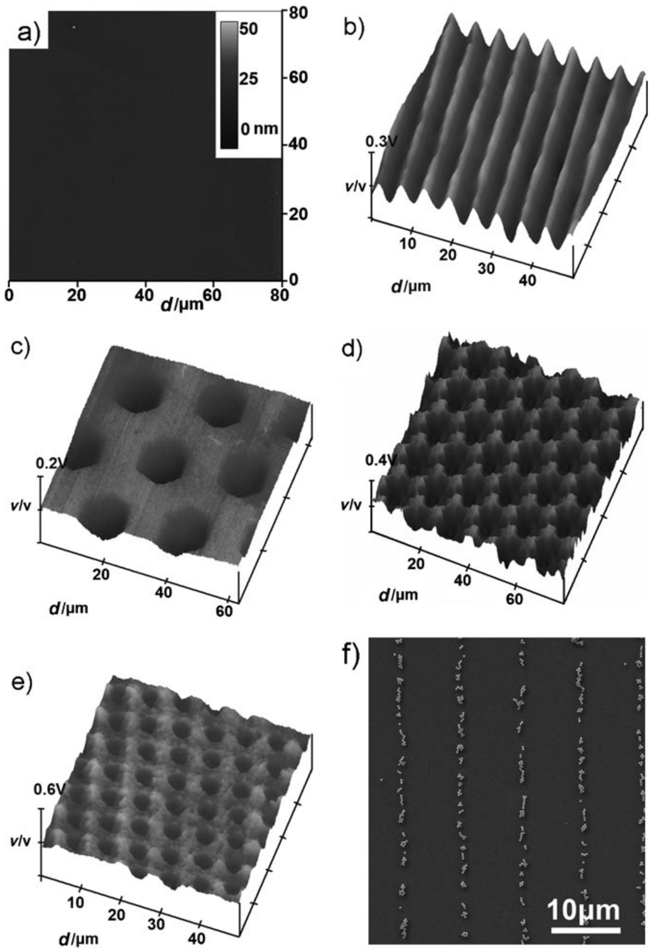

Figure 2. a) AFM and b–e) KFM images showing the topography and surface potential differences on a PMMA thin film after selective discharging by a hydrogel stamp; f) SEM image showing the adsorption of silica microbeads on the obtained charge patterns.

chemistry[6] to produce micro- or nanostructures of metals, as shown in Figure 1 f.

It is not necessary that the electrets are supported on a conductive Si substrate to be charged by an electric field as shown in Figure 1 c,d, because many other charging methods, such as a simple contact electrification process, could be applied in this step for uniformly charging the electrets (see the Supporting Information). Herein, we chose Si wafer supported PMMA films as electrets to characterize the high-resolution charge patterns by Kelvin probe force microscopy (KFM), a tool to measure electrostatic potential through an electric cycle. Atomic force microscopy (AFM) images (Figure 2 a) show the surface topography of PMMA film after the selectively discharging, and the flat surface morphology indicates that there are no observable differences in topography before and after the hydrogel stamping operation. The KFM images (Figure 2 b–e) show a set of surface potential changes after the selective discharging process. From these images, we clearly find that the technique can generate various electrostatic charge patterns on PMMA thin film electrets, and the different geometries and length scales are determined by the features of the as-used agarose hydrogel stamp with resolution around 150 nm. Figure 2 f shows a SEM image of silica microbeads adsorbed on the charged area of electrets, and this phenomenon, as widely applied in photocopier and nanoxerography, is used to demonstrate one of the applications of the as-prepared charge patterns.

The charge patterns measured by KFM or scanning electric potential microscopy (SEPM) demonstrate great progress in the study of electrostatics on dielectrics and other solids. However, as described by Liu and Bard,[8] the net charge on a dielectric surface is the sum of the electronic and the ionic charge, and the nature of the charge cannot be distinguished by simply measuring the total surface charge or surface potential. They developed a chemical approach, so-called “single-electrode” electrochemistry or electrostatic electrochemistry, to selectively detect electrons (rather than ions) on the surface of dielectrics. By carrying out chemical redox reactions such as metal deposition, ion reduction and chemiluminescence on the rubbed teflon, they identified electrons as the main components in contact electrification. Herein, we utilize their developments to fabricate metallic micro- or nanostructures by reducing metal ions on the charge patterns (mainly electrons).

Figure 3 shows SEM images of different metallic micro- and nanostructures on PMMA by reducing metal ions with patterns of charge. Although the charge density in PMMA

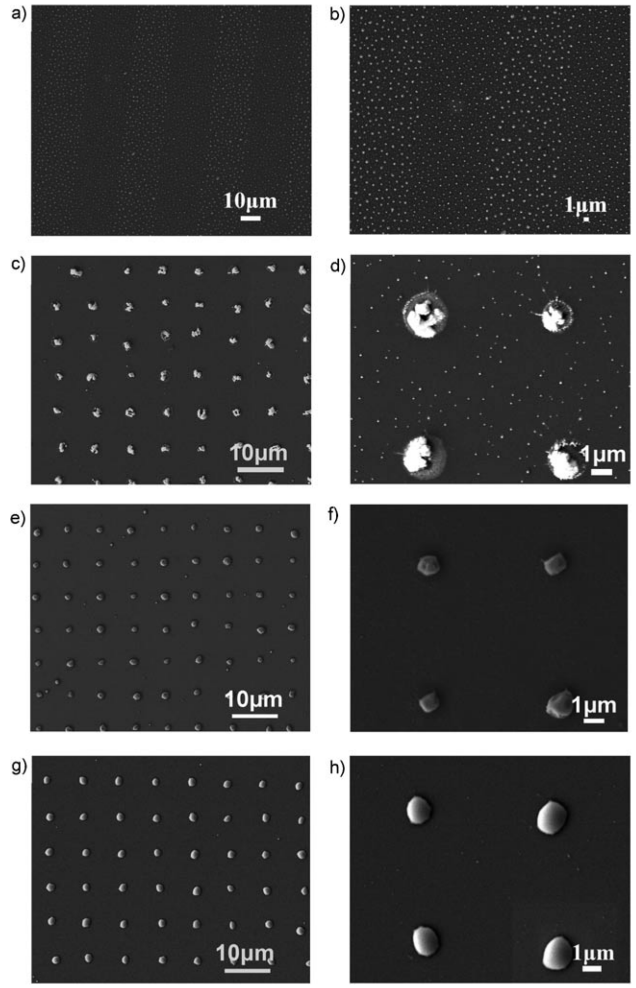

Figure 3. SEM images of different metal micro- and nanostructures reduced by the patterns of electrostatic charge. The figures on the right (b, d, f, h) are magnified views of the corresponding left of set images (a, c, e, g). a–d) Ag (reduced from Ag^+); e,f) Ni (from Ni^{2+}); g,h) Cu (from Cu^{2+}).

using the electric field charging method should be higher than that charged by contact electrification, the total number of charges or electrons on electrets is still rather small. To obtain observable and regular metallic microstructures on the dielectric, we intentionally dissolved the metal ion salts in ethanol rather than in water. The aqueous solution of metal salts can leave some stains on PMMA during evaporation. Especially when a small volume of solution is dropped onto charge patterns, the coffee-ring-like stains will inevitably be confused with as-reduced metallic microstructures. Herein, the PMMA electrets supported on silicon were uniformly dipped into ethanol solution; since ethanol can ensure the ionization of these metal salts without dissipating the charges too quickly ($pK_{\text{a water}} = 14$, $pK_{\text{a ethanol}} = 16$), metal ions can be easily reduced into metallic microstructures over a large area.

Figure 3a–d shows the reduction of Ag from $AgNO_3$ solution in ethanol, and Figure 3e–h shows the reduction of Ni and Cu from their salts in ethanol. From these Figures, we can clearly find that Ag microstructures corresponding to the features on agarose stamp can be formed on charged area on PMMA, whereas on the hydrogel directly contacted area where charge should be dissipated, there are still some noticeable Ag nanoparticles. For nickel and copper, the microstructures look much more regular, and the nanoparticles on the discharged area are nearly negligible. We attribute this phenomenon to the reduction of Ag^+ being much easier than that of Cu^{2+} and Ni^{2+} (the reduction potential of Ag^+ is much lower), therefore the residual charges in PMMA after hydrogel discharging can induce the reduction of Ag^+ rather than Cu^{2+} and Ni^{2+}.

To confirm the reduction of metal (e.g. copper) on the patterns of electrostatic charge, we used the auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) to analyze the as-prepared microstructures. As shown in Figure 4a, an AES depth profile was measured to analyze

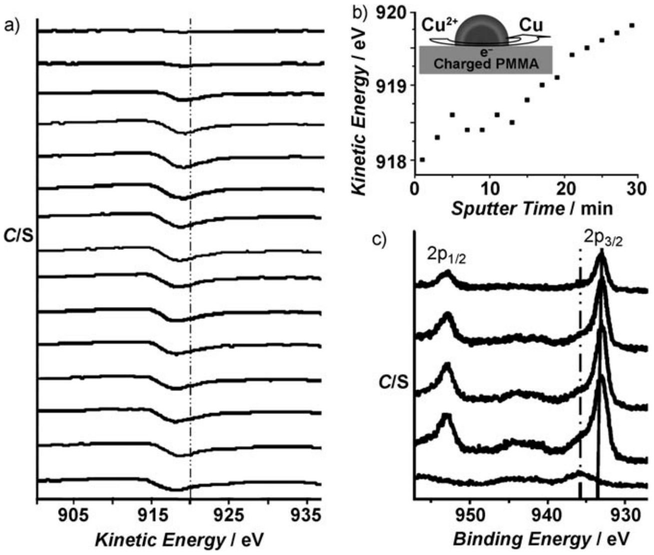

Figure 4. a,b) Auger electron spectroscopy and c) X-ray photoelectron spectroscopy analysis of the as-prepared copper microbeads.

the copper microbeads by sputtering the sample with Ar^+. Following the sputtering time (from bottom to top as in Figure 4a), the auger spectra are shifted towards higher kinetic energy from 918.0 eV to 919.8 eV[22] (the values of characteristic auger spectra peaks are shown in Figure 4b, which means the transition from Cu^{2+} to Cu. We demonstrate the phenomenon with a cartoon image in the inset in Figure 4b, which indicates that the inner core of the microstructure is made of as-reduced Cu and the outer ring remains in its oxidized state. This hypothesis was further verified by XPS results (Figure 4c), which shows a shift of the $Cu(2p_{3/2})$ peaks from 935.3 eV to 932.9 eV and a decrease of shake-up peaks.[23] The electrons on the surface of the electrets can reduce Cu^{2+} to Cu in the inner core, while the embedded electrons[2,8] in the electrets attract cupric ions from the ethanolic solution through a xerographic effect and achieve the outer ring of the as-prepared metallic microstructures.

In conclusion, we have demonstrated a very simple and inexpensive procedure to transfer and print "water" or humidity to induce the charge dissipation on solid surfaces.

Electrostatic charges on many dielectrics, particularly for those widely explored electrets fabricated by contact electrification, can be uniquely patterned by using this method (a demonstration of the patterning method on contact electrification system is shown in Figure S1 in the Supporting Information). Since high-resolution charge patterns are extremely useful in data storage, nanocomponent optoelectronics and self-assembly systems, the method of patterning electrostatic charges through selectively discharging shows a prominent role in exploring new application of electrets.

It is worthy of note that the mechanism of discharging electrostatics by water is not explained in detail herein. As one of the main controversial factors for contact electrification, the role of water during charging and discharging of electrets remains unclear and debatable. Both electrons and ions can be affected by water with different explanations;[24,25] even for dipolar electrets, water can have a significant impact on their properties.[26] Herein, we chose hydrogel rather than other stamps[27] because the patterned hydrogel stamp can selectively transfer water onto electrets for discharging either by spreading of electrons (increasing the surface conductivity), or by transporting ions from the contacted area to outside through diffusion, and it does not bring new disputes into the field. This paper is aimed at providing a simple approach for patterning of high-resolution electrostatic charges, and further investigations are necessary to solve puzzles such as contact electrification in electrostatics.

Experimental Section

All materials and chemicals were purchased commercially and used as received. PMMA and silica microspheres were purchased from Aldrich. Other chemical reagents were purchased from Sinopharm Chemical Reagent Beijing Co. All AFM images were recorded using a Veeco D3100 instrument and SEM images were recorded with a JEOL 7401 microscope. XPS spectra were obtained with a Thermo-Fisher ESCALAB 250 system using monochromated Al Kα 150W (Spot size = 500 μm, Pass Energy = 200 eV for survey; 30 eV for high-resolution scans). AES spectra were measured in a ULVAC-PHI 700 SAM system. For AES analysis, the electron beam energy was 10.0 keV. During the depth-profile analysis, the Ar ion beam sputter rate was set at $8\,\mathrm{nm\,min^{-1}}$ for SiO_2.

Fabrication of hydrogel stamp: A hot, degassed 5% w/w solution of agarose (Biowest agarose) in pure water was cast against a PDMS stamp with the desired pattern on its surface. The agarose stamp was cooled to room temperature until it was well gelated, and then gently peeled off. The hydrogel stamp was patterned with the negative of the array of features in the PDMS stamp.

Patterning of charge on PMMA film: A 2% solution of PMMA in chlorobenzene was spin-coated at 6000 rpm on a Si wafer to fabricate a thin film of PMMA electret with a thickness of around 100 nm. The silicon wafer with PMMA thin film was cut into $0.5\,\mathrm{cm^2}$ squares. The surface of PMMA film was covered with a piece of aluminum foil, which served as another electrode. A Keithley 2400 source meter was used to apply pulse current. After applying voltage at $10\,\mathrm{kV\,cm^{-1}}$ for 20 s, the PMMA film was removed from the power source and conformally contacted with the agarose hydrogel stamp for 5 s.

Adsorption of nanoparticles: The charged PMMA film was immersed into a 0.5% w/v suspension of silica microspheres (500 nm) in ethanol for 30 s and quickly rinsed with ethanol to remove the loosed attached part.

Reduction of metal ions: The PMMA electrets with patterned charge were immersed into ethanolic solution containing different metal ion salts for 20 s, and then washed with ethanol. The solutions of $Ni(CH_3COO)_2{\cdot}4H_2O$, $CuSO_4{\cdot}5H_2O$, and $AgNO_3$ in ethanol were diluted to half of their saturated capacity.

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